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D.H. Katayama

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D.H. Katayama

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(617) 377-4042

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# Comment on: "Observation of strong Rydberg-valence mixing in the $E^3\Sigma_u^-$ state of $O_2$ by 3+1 multiphoton ionization photoelectron spectroscopy"

D. H. Katayama

Air Force Geophysics Laboratory (LIU), Hanscom Air Force Base, Massachusetts 01731

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A recent paper by Miller *et al.* on the 3 + 1 MPI photoelectron spectrum of  $O_2$  via its  $E^3\Sigma_u^-$  state shows that the so-called "longest" band has a strongly mixed Rydberg-valence character. In order to prevent confusion it should be noted that this  $E$  state was relabeled  $B'^3\Sigma_u^-$  because of this mixture and its formation from the upper state of the well known Schumann-Runge bands; namely,  $B^3\Sigma_u^-$ . Based on theoretical calculations, the  $B'^3\Sigma_u^-$  state was predicted to have as its first three vibrational levels, the longest, "second," and "third" bands at 1244, 1206, and 1172 Å, respectively. Miller *et al.* also show that their MPI data agree with the longest band being a (0,0) band which they

report is in contrast to the original assignment of Ogawa *et al.* who assigned it as (1,0). It is necessary to point out that the original assignment of Ogawa *et al.* was changed on the basis of a reanalysis of the spectroscopic data. This reanalysis is discussed in the last paragraph of Ref. 5, where we showed that the longest, second, and third bands should indeed be the (0,0), (1,0), and (2,0) bands of the  $B'^3\Sigma_u^- - X^3\Sigma_g^-$  transition. We also reassigned the 1269 Å band as (0,1) of this band system. More recent work on the  $O_2$  absorption spectrum at high temperature supports these vibrational assignments. There is, therefore, agreement among the theoretical, spectroscopic, and MPI studies as to

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the vibrational assignment of the longest band of oxygen.

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